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Continuous preparation of organosilanes

The invention relates to a process for the continuous preparation of organosilanes by hydrosilylation in the presence of an iridium compound as catalyst and free diene as cocatalyst.

Substituted alkylsilanes are of tremendous economic importance in many fields. They are used, for example, as adhesion promoters or as crosslinkers.

The platinum- or rhodium-catalyzed hydrosilylation of unsaturated compounds has been widely studied in the past. The product yields are often very low, being only 20-45%, which is attributable to considerable secondary reactions.

Iridium catalysts containing diene ligands are, according to US-A-4658050, used in the hydrosilylation of allyl compounds by means of alkoxy-substituted silanes. JP-A-07126271 describes the hydrosilylation of allyl halides using chlorodimethylsilane in the presence of iridium catalysts containing diene ligands. Disadvantages of these processes are either moderate yields, an uneconomically high catalyst concentration and/or a very short catalyst life. Although EP-A-1156052 and DE-C-10053037 describe the addition of additional diene ligands to increase the catalyst life, the processes in all cases mentioned are batch processes which are subject to very unfavorable preconditions both from an economic point of view and an engineering and safety point of view because of the strongly exothermic character of hydrosilylation reactions (risk of the reaction becoming "dormant" and later starting up again with a sudden, extremely high

generation of heat and pressure).

It is therefore an object of the invention to develop a process which gives high product yields and purities and, in particular, takes account of the aspects of economic and especially engineering and safety considerations. This object was able to be achieved by the present invention.

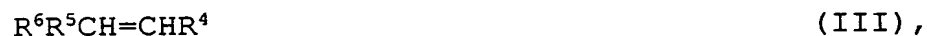
The invention provides a process for the continuous preparation of a silane of the formula I



which comprises continuously reacting a silane of the formula II



with an alkene of the formula III



in the presence of an iridium compound of the formula IV as catalyst



and free diene as cocatalyst, where

R^1 , R^2 , R^3 are each a monovalent Si-C-bonded, unsubstituted or halogen-substituted C_1 - C_{18} -hydrocarbon radical, a chlorine atom or a C_1 - C_{18} -alkoxy radical,

R^4 , R^5 , R^6 are each a hydrogen atom, a monovalent C_1 - C_{18} -hydrocarbon radical which may be unsubstituted

or bear F, Cl, OR, NR'₂, CN or NCO atoms/groups as substituents, a chlorine atom, a fluorine atom or a C₁-C₁₈-alkoxy radical, where in each case 2 radicals R⁴, R⁵, R⁶ together with the carbon atoms to which they are bound may form a cyclic radical, R is a hydrogen atom or a monovalent C₁-C₁₈-hydrocarbon radical and diene is a C₄-C₅₀-hydrocarbon compound which may be unsubstituted or bear F, Cl, OR, NR₂, CN or NCO atoms/groups as substituents and has at least two ethylenic C=C double bonds, with the reaction temperature being 30-200°C and the reaction pressure being 0.11-50.0 Mpa.

The continuous process gives the silene of the formula I in high yields and excellent purity.

In this process, the target products of the formula I are obtained in yields of from at least 95% up to 98% when using very small amounts of catalyst. Depending on the field of application, work-up by distillation can therefore be dispensed with.

The process is easy to control and can be carried out safely.

Suitable engineering embodiments for carrying out the process are all customary reactors for carrying out reactions continuously, i.e., for example, tube and loop reactors and also continuously operated stirred reactors.

In terms of the order in which the reaction components are introduced, all conceivable combinations are possible; in particular, the components can be partly

premixed before introduction into the reactor. The catalyst is preferably not present in an environment comprising an excess of silane of the formula II over the alkene of the formula III, since this can otherwise display deactivation.

C_1 - C_{18} -hydrocarbon radicals R^1 , R^2 , R^3 are preferably alkyl, alkenyl, cycloalkyl or aryl radicals. R^1 , R^2 , R^3 preferably have not more than 10, in particular not more than 6, carbon atoms. R^1 , R^2 , R^3 are preferably linear or branched C_1 - C_6 -alkyl radicals or C_1 - C_6 -alkoxy radicals. Preferred halogen substituents are fluorine and chlorine. Particularly preferred radicals R^1 , R^2 , R^3 are methyl, ethyl, methoxy, ethoxy, chlorine, phenyl and vinyl.

Hydrocarbon radicals R^4 , R^5 , R^6 are preferably alkyl, alkenyl, cycloalkyl or aryl radicals. It is preferred that not more than one of R^4 , R^5 , R^6 is an alkoxy radical. R^5 , R^6 preferably have not more than 10, in particular not more than 6, carbon atoms. R^5 , R^6 are preferably linear or branched C_1 - C_6 -alkyl radicals or C_1 - C_6 -alkoxy radicals. Particularly preferred radicals R^5 , R^6 are hydrogen, methyl, ethyl, chlorine and phenyl.

The hydrocarbon radical R^4 preferably has not more than 6, in particular not more than 2, carbon atoms. Particularly preferred radicals R^4 are hydrogen, methyl, ethyl.

The hydrocarbon radical R preferably has not more than 6, in particular not more than 2, carbon atoms.

The hydrocarbon compounds used as diene may comprise not only the molecular units containing ethylenic $C=C$

double bonds but also alkyl, cycloalkyl or aryl units. The dienes preferably have from 6 to 12 carbon atoms. Preference is given to monocyclic or bicyclic dienes. Preferred examples of dienes are butadiene, 1,3-
5 hexadiene, 1,4-hexadiene, 1,5-hexadiene, isoprene, 1,3-cyclohexadiene, 1,3-cyclooctadiene, 1,4-cyclooctadiene, 1,5-cyclooctadiene and norbornadiene.

10 The diene in the catalyst of the formula IV and the free diene serving as cocatalyst can be identical or different. Preference is given to the two dienes being identical.

15 In a particularly preferred case, the catalyst of the formula IV used is $[(\text{cycloocta-1c,5c-diene})\text{IrCl}]_2$ and the cocatalyst used is 1,5-cyclooctadiene.

20 The alkene of the formula III is preferably used in an excess of from 0.01 to 100 mol% of II, particularly preferably from 0.1 to 10 mol%, based on the silane component of the formula II. The iridium compound of the formula IV is preferably present in a concentration of from 1×10^{-6} to 1×10^{-1} mol%, in particular from 1×10^{-4} to 1×10^{-2} mol%, based on the silane component of the
25 formula II. The diene as cocatalyst is preferably added in a concentration of from 1×10^{-6} to 1 mol%, in particular from 1×10^{-3} to 1×10^{-1} mol%, based on the silane component of the formula II as cocatalyst.

30 The process can be carried out in the presence or absence of aprotic solvents. If aprotic solvents are used, solvents or solvent mixtures having a boiling point or boiling range up to 120°C at 0.1 MPa are preferred. Examples of such solvents are ethers such as
35 dioxane, tetrahydrofuran, diethyl ether, diisopropyl

ether, diethylene glycol dimethyl ether; chlorinated hydrocarbons such as dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, trichloroethylene; hydrocarbons such as pentane, n-hexane, 5 hexane isomer mixtures, heptane, octane, naphtha, petroleum ether, benzene, toluene, xylenes; ketones such as acetone, methyl ethyl ketone, diisopropyl ketone, methyl isobutyl ketone (MIBK); esters such as ethyl acetate, butyl acetate, propyl propionate, ethyl 10 butyrate, ethyl isobutyrate; carbon disulfide and nitrobenzene, or mixtures of these solvents.

The target product of the formula I can also be used as aprotic solvent in the process. This process variant is 15 preferred.

The process is preferably carried out at a reaction temperature of 60-100°C, particularly preferably 75-85°C. The reaction pressure is preferably 20 0.2-1.5 MPa, particularly preferably 0.4-0.5 MPa.

For example, the reaction components of the formula II as one feed stream and the reaction components of the formula III together with iridium catalyst of the 25 formula IV, if appropriate in admixture with the diene, as second feed stream are fed continuously into a loop reactor. In another variant, the reactor is started up by initially charging it with the target product of the formula I or an abovementioned solvent together with 30 catalyst of the formula IV and, if appropriate, diene and continuously feeding a mixture of component III and, if appropriate, diene as one feed stream and the component of the formula II as second feed stream continuously into the reactor. The mean residence times 35 of the reactor contents are preferably from 5 to

60 minutes, in particular from 10 to 40 minutes, particularly preferably from 25 to 30 minutes.

- 5 The meanings of all the symbols in the formulae above are in each case independent of one another.

In the following examples, all concentrations and percentages are by weight, all pressures are 0.10 MPa (abs.) and all temperatures are 20°C unless indicated otherwise.

Example 1

Dimethylchlorosilane as one feed stream and a mixture
15 of 2.7×10^{-3} mol% of di- μ -chlorobis[(cycloocta-1c,5c-diene)iridium(I)] and 7×10^{-1} mol% of 1,5-cyclooctadiene in allyl chloride as a second feed stream were fed in a molar ratio of silane:allyl chloride mixture of 1:1.05 at a rate of 2.8 l/h (based on the
20 total volume of the components introduced) via separate metering pumps into a loop reactor maintained at 80°C under a pressure of 0.4 MPa and having a volume of 1.4 l. After working up the crude mixture by distillation using a thin film evaporator to separate
25 off the catalyst and the excess of allyl chloride, chloro(3-chloropropyl)dimethylsilane was obtained in a yield of 95% and a purity of > 99% based on the silane.

Example 2

30 Example 1 was repeated with the modification that the reactor was operated at 50°C and a pressure of 0.2 MPa and the reactants were fed in at a rate of 2.1 l/h (based on the total volume of the components introduced). After working up the crude mixture by

distillation using a thin film evaporator to separate off the catalyst and the excess of allyl chloride, chloro(3-chloropropyl)dimethylsilane was obtained in a yield of 95% and a purity of > 99% based on the silane.

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Example 3

Example 1 was repeated with the modification that the reactor was operated at 100°C and a pressure of 1.0 MPa and the reactants were fed in at a rate of 5.6 l/h (based on the total volume of the components introduced). After working up the crude mixture by distillation using a thin film evaporator to separate off the catalyst and the excess of allyl chloride, chloro(3-chloropropyl)dimethylsilane was obtained in a yield of 95% and a purity of > 99% based on the silane.

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Example 4

Example 1 was repeated with the modification that the reactor was operated at 130°C and a pressure of 1.0 MPa and the reactants were fed in at a rate of 5.6 l/h (based on the total volume of the components introduced). After working up the crude mixture by distillation using a thin film evaporator to separate off the catalyst and the excess of allyl chloride, chloro(3-chloropropyl)dimethylsilane was obtained in a yield of 95% and a purity of > 99% based on the silane.

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Example 5

Example 1 was repeated with the modification that the reactants were fed in in a molar ratio of silane:allyl chloride mixture of 1:1. After working up the crude mixture by distillation using a thin film evaporator to separate off the catalyst, chloro(3-chloropropyl)-dimethylsilane was obtained in a yield of 95% and a

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purity of > 99% based on the silane.

Example 6

Example 1 was repeated with the modification that the
5 reactants were fed in in a molar ratio of silane:allyl
chloride mixture of 1:1.3. After working up the crude
mixture by distillation using a thin film evaporator to
separate off the catalyst and the excess of allyl
chloride, chloro(3-chloropropyl)dimethylsilane was
10 obtained in a yield of 95% and a purity of > 99% based
on the silane.

Example 7

Example 1 was repeated with the modification that 1×10^{-4}
15 mol% of di- μ -chlorobis[(cycloocta-1c,5c-diene)-
iridium(I)] and 1×10^{-3} mol% of 1,5-cyclooctadiene were
used. After working up the crude mixture by
distillation using a thin film evaporator to separate
off the catalyst and the excess of allyl chloride,
20 chloro(3-chloropropyl)dimethylsilane was obtained in a
yield of 95% and a purity of > 99% based on the silane.

Example 8

Example 1 was repeated with the modification that
25 toluene was placed in the reactor as solvent before
commencement of the metered addition. After working up
the crude mixture by distillation using a thin film
evaporator to separate off the catalyst and the excess
of allyl chloride, chloro(3-chloropropyl)dimethylsilane
30 was obtained in a yield of 95% and a purity of > 99%
based on the silane.

Example 9

Example 1 was repeated with the modification that a tube reactor was used in place of the loop reactor. After working up the crude mixture by distillation
5 using a thin film evaporator to separate off the catalyst and the excess of allyl chloride, chloro(3-chloropropyl)dimethylsilane was obtained in a yield of 95% and a purity of > 99% based on the silane.

10 **Example 10**

Example 1 was repeated with the modification that the high-boiling residue obtained in the isolation of the product was used in place of a freshly prepared catalyst/cocatalyst mixture. After working up the crude
15 mixture by distillation using a thin film evaporator to separate off the catalyst and the excess of allyl chloride, chloro(3-chloropropyl)dimethylsilane was obtained in a yield of 95% and a purity of > 99% based on the silane.